Claims

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[1] A substituted Sym-triindole derivative represented by the following general formula (1)

[formula 1]

$$R_{1}$$
 $R_{2}$ 
 $R_{3}$ 
 $R_{4}$ 
 $R_{4}$ 
 $R_{4}$ 
 $R_{5}$ 
 $R_{4}$ 
 $R_{5}$ 
 $R_{1}$ 
 $R_{5}$ 
 $R_{4}$ 
 $R_{1}$ 
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 $R_{1}$ 
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 $R_{4}$ 
 $R_{5}$ 
 $R_{4}$ 
 $R_{5}$ 
 $R_{5}$ 

(wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each independently hydrogen, halogen, C1-C6 alkyl group, C1-C6 haloalkyl group, substituted C2-C6 alkenyl group, C2-C6 alkenyl group, substituted C2-C6 alkenyl group, C2-C6 alkynyl group, substituted C2-C6 alkynyl group, hydroxyl group, C1-C6 alkoxy group, aryloxy group, amino group, mono-substituted amino group, disubstituted amino group, acylamino group, mercapto group, C1-C6 alkylsulfenyl group, C1-C6 haloalkylsulfenyl group, arylsulfinyl group, C1-C6 haloalkylsulfinyl group, aralkylsulfenyl group, arylsulfinyl group, arylsulfinyl group, substituted arylsulfinyl group, aralkylsulfenyl group, arylsulfinyl group, substituted arylsulfinyl group, substituted arylsulfinyl

group, C1-C6 alkylsulfonyl group, C1-C6 haloalkylsulfonyl group, arylsulfonyl group, substituted arylsulfonyl group, sulfonic acid group (hydroxysulfonyl group), aryl group, substituted aryl group, cyano group, nitro group, formyl group, acyl group, carboxyl group, C1-C6 alkoxycarbonyl group, carbamoyl group, N-mono-substituted carbamoyl group, N,N-disubstituted carbamoyl group, hydrazonomethyl group (-CH=N-NH2 group), N-mono-substituted hydrazonomethyl group, N,N-disubstituted hydrazonomethyl group, oximemethyl group (hydroxyiminomethyl group), C1-C6 alkoxyiminomethyl group, or aryloxyiminomethyl group; R<sub>5</sub> is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group, or aryl C1-C6 alkyl group; in no event, all of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen simultaneously).

15 [2] A process for producing a substituted Sym-triindole derivative represented by the following general formula (1)

[formula 3]

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$$\begin{array}{c|cccc}
R_1 & R_2 & R_3 & R_4 & R_4 & R_5 & R_4 & R_5 & R_1 & R_5 & R_4 & R_2 & R_3 & R_3 & R_2 & R_3 & R_3 & R_2 & R_3 & R_3 & R_3 & R_2 & R_3 & R_3 & R_3 & R_4 & R_5 & R_4 & R_5 &$$

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(wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently hydrogen, halogen, C1-C6 alkyl group, C1-C6 haloalkyl group, substituted C1-C6 alkyl group, C2-C6 alkenyl group, substituted C2-C6 alkenyl group, C2-C6 alkynyl group, substituted C2-C6 alkynyl group, hydroxyl group, C1-C6 alkoxy group, aryloxy group, amino group, mono-substituted amino group, substituted amino group, acylamino group, mercapto group, C1-C6 alkylsulfenyl group, C1-C6 haloalkylsulfenyl group, aralkylsulfenyl group, arylsulfenyl group, substituted arylsulfenyl group, C1-C6 alkylsulfinyl group, C1-C6 haloalkylsulfinyl group, arylsulfinyl group, substituted arylsulfinyl group, C1-C6 alkylsulfonyl group, C1-C6 haloalkylsulfonyl group, arylsulfonyl group, substituted arylsulfonyl group, 'sulfonic acid group (hydroxysulfonyl group), aryl group, substituted aryl group, cyano group, nitro group, formyl group,

acyl group, carboxyl group, C1-C6 alkoxycarbonyl group, carbamoyl group, N-mono-substituted carbamoyl group, N,N-disubstituted carbamoyl group, hydrazonomethyl group (-CH=N-NH2 group), N-mono-substituted hydrazonomethyl group, N,N-disubstituted hydrazonomethyl group, oximemethyl group (hydroxyiminomethyl group), C1-C6 alkoxyiminomethyl group, or aryloxyiminomethyl group;  $R_5$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group, or aryl C1-C6 alkyl group; in no event, all of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen simultaneously), which process comprises reacting a substituted oxyindole represented by the following general formula (2)

[formula 2]

10

$$\begin{array}{c|c}
R_3 & R_4 \\
R_2 & N \\
R_1 & R_5
\end{array}$$
(2)

(wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  have the same definitions as given above) with a phosphorus oxyhalide.

[3] A Sym-triindole derivative represented by the following general formula (3)

## [formula 4]

$$R_6$$
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_6$ 
 $R_6$ 
 $R_6$ 

(wherein  $R_5$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group, or aryl C1-C6 alkyl group; and  $R_6$  is hydrogen, formyl group, cyano group, C1-C6 alkoxycarbonyl group, dicyanovinyl group, aryl group or substituted aryl group).

[4] A process for producing a Sym-triindole derivative represented by the following general formula (7)

[formula 8]

5

$$R_7$$
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 

(wherein  $R_5$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group; and  $R_7$  is hydrogen, formyl group, cyano group, C1-C6 alkoxycarbonyl group, aryl group or substituted aryl group), which process comprises reacting an N-substituted-5-halo-oxyindole represented by the following general formula (4)

[formula 5]

$$\begin{array}{ccc}
X & & & \\
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(wherein  $R_5$  has the same definition as given above; and X is halogen) with a phosphorus oxyhalide to obtain an N-substituted-5-halo-triindole derivative represented by the following general formula (5)

[formula 6]

(wherein  $R_5$  and X have the same definitions as given above) and further reacting it with a boric acid compound represented by the following general formula (6)

[formula 7]

$$R_7$$
  $OR_a$  (6)

- $R_{b}$  are each independently hydrogen atom, C1-C6 alkyl group or optionally substituted phenyl group and may be combined to each other to form a ring).
- [5] A process for producing a Sym-triindole derivative rep-10 resented by the following general formula (7)

[formula 11]

$$R_7$$
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 
 $R_7$ 

(wherein  $R_5$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group; and  $R_7$  is hydrogen, formyl group, cyano group, C1-C6 alkoxycarbonyl group, aryl group or substituted aryl group), which process comprises reacting an N-substituted-5-halo-triindole derivative represented by the following general formula (5)

[formula 9]

(wherein  $R_5$  has the same definition as given above; and X is halogen) with a boric acid compound represented by the fol-

lowing general formula (6)

[formula 10]

$$R_7$$
  $OR_a$  (6)  $OR_b$ 

(wherein  $R_7$  has the same definition as given above; and  $R_a$  and  $R_b$  are each independently hydrogen atom, C1-C6 alkyl group or optionally substituted phenyl group and may be combined to each other to form a ring).

[6] A process for producing an N-substituted-5-halo-triindole derivative represented by the following general formula (5)

10 [formula 13]

$$X$$
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 

(wherein  $R_5$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group; and X is halogen), which process comprises reacting an N-

substituted-5-halo-oxyindole represented by the following general formula (4)

[formula 12]

$$\begin{array}{ccc}
X & & & \\
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5

(wherein  $R_5$  and X have the same definitions as given above) with a phosphorus oxyhalide.

[7] A process for producing a Sym-triindole derivative represented by the following general formula (10)

[formula 16]

$$R_8$$
 $R_9$ 
 $R_8$ 
 $R_8$ 
 $R_8$ 
 $R_8$ 
 $R_8$ 
 $R_8$ 
 $R_9$ 
 $R_8$ 
 $R_8$ 
 $R_9$ 
 $R_8$ 
 $R_8$ 

(wherein  $R_5$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group;  $R_8$ 

is hydrogen or cyano group; and R<sub>9</sub> is cyano group, carboxylic acid group, C1-C6 alkoxycarbonyl group, aryl group or substituted aryl group), which process comprises reacting a triindole derivative represented by the following general formula (8)

[formula 14]

5

OHC 
$$R_5$$
  $N$   $R_5$   $R_5$  (8)

(wherein  $R_5$  has the same definition as given above) with a methylene compound represented by the general formula (9)

[formula 15]

$$R_8 \cap R_9$$
 (9)

- 10 (wherein  $R_8$  and  $R_9$  have the same definitions as give above).
  - [8] A Sym-triindole vinyl derivative represented by the following general formula (11)

[formula 17]

$$R_{10} \longrightarrow R_{10}$$

(wherein  $R_8$  is hydrogen or cyano group;  $R_9$  is cyano group, carboxylic acid group, C1-C6 alkoxycarbonyl group, aryl group or substituted aryl group; and  $R_{10}$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group).

[9] A process for producing a Sym-triindole derivative represented by the following general formula (11)

## [formula 22]

$$R_{10}$$
 $R_{10}$ 
 $R_{10}$ 

(wherein  $R_8$  is hydrogen or cyano group;  $R_9$  is cyano group,

carboxylic acid group, C1-C6 alkoxycarbonyl group, aryl group or substituted aryl group; and  $R_{10}$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group), which process comprises reacting an oxyindole compound represented by the following general formula (12)

[formula 18]

10

(wherein  $R_{10}$  has the same definition as given above and X is halogen) with a phosphorus oxyhalide to obtain a Sym-halotriindole derivative represented by the following general formula (13)

[formula 19]

$$\begin{array}{c|c}
R_{10} & X \\
X & R_{10}
\end{array}$$

$$\begin{array}{c}
R_{10} & X \\
X & X
\end{array}$$

$$\begin{array}{c}
X & X \\
X & X
\end{array}$$

$$\begin{array}{c}
X & X \\
X & X
\end{array}$$

$$\begin{array}{c}
X & X \\
X & X
\end{array}$$

$$\begin{array}{c}
X & X \\
X & X
\end{array}$$

(wherein  $R_{10}$  and X have the same definitions as given above),

subjecting it to formylation with a formylating agent in the presence of butyllithium to obtain a Sym-formyltriindole derivative represented by the following general formula (14)

[formula 20]

OHC 
$$R_{10}$$
  $R_{10}$   $R_{10}$ 

 $_{10}$  (wherein  $R_{10}$  has the same definition as given above), and reacting it with a methylene compound represented by the following general formula (9)

[formula 21]

$$R_8 \stackrel{\frown}{R}_9$$
 (9)

(wherein  $R_8$  and  $R_9$  have the same definitions as given above).

10 [10] A process for producing a Sym-triindole derivative represented by the following general formula (11)

[formula 25]

$$R_{10} \xrightarrow{R_{10}} R_{10}$$

(wherein  $R_{\theta}$  is hydrogen or cyano group;  $R_{\theta}$  is cyano group, carboxylic acid group, C1-C6 alkoxycarbonyl group, aryl group or substituted aryl group; and  $R_{10}$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group), which process comprises reacting a Sym-formyltriindole derivative represented by the following general formula (14)

#### [formula 23]

5

(wherein  $R_{10}$  has the same definition as given above) with a 10 methylene compound represented by the following general for-

mula (9)

5

[formula 24]

$$R_8 \stackrel{\frown}{R}_9$$
 (9)

(wherein  $R_8$  and  $R_9$  have the same definitions as given above).

[11] A process for producing a Sym-formyltriindole derivative represented by the following general formula (14)

[formula 27]

OHC 
$$R_{10}$$
  $R_{10}$   $R_{10}$ 

(wherein  $R_{10}$  is C2-C12 alkyl group, C2-C12 substituted alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group), which process comprises subjecting a Sym-halo-triindole derivative represented by the following general formula (13)

[formula 26]

$$\begin{array}{c|c}
 & X \\
 & R_{10} \\
 & N \\
 & R_{10}
\end{array}$$

$$\begin{array}{c}
 & X \\
 & R_{10} \\
 & X
\end{array}$$

$$\begin{array}{c}
 & X \\
 & R_{10} \\
 & X
\end{array}$$

$$\begin{array}{c}
 & X \\
 & X
\end{array}$$

$$\begin{array}{c}
 & X \\
 & X
\end{array}$$

(wherein  $R_{10}$  has the same definition as given above and X is halogen), to formylation with a formylating agent in the presence of butyllithium.

[12] A Sym-triindole derivative represented by the following
5 general formula (15)

## [formula 28]

$$R_{10}$$
 $R_{10}$ 
 $R_{10}$ 
 $R_{10}$ 
 $R_{10}$ 
 $R_{11}$ 
 $R_{11}$ 

(wherein  $R_{10}$  is C2-C12 alkyl group, C2-C12 substituted alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group; and  $R_{11}$  is aryl group or substituted aryl group).

[13] A process for producing a Sym-triindole derivative represented by the following general formula (15)

## [formula 31]

$$R_{10}$$
  $R_{10}$   $R_{10}$   $R_{10}$   $R_{10}$   $R_{11}$ 

(wherein  $R_{10}$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group; and  $R_{11}$  is aryl group or substituted aryl group), which process comprises reacting a Sym-halo-triindole derivative represented by the following general formula (13)

# [formula 29]

5

$$\begin{array}{c|c}
R_{10} & X \\
X & R_{10} \\
N & X
\end{array}$$

$$\begin{array}{c}
R_{10} & X \\
X & X
\end{array}$$

$$\begin{array}{c}
X & X \\
X & X
\end{array}$$

$$\begin{array}{c}
X & X \\
X & X
\end{array}$$

(wherein  $R_{10}$  has the same definition as given above and X is halogen) with an acetylene derivative represented by the following general formula (16)

[formula 30]

$$R_{11} - R_{12}$$
 (16)

- 5 (wherein  $R_{11}$  has the same definition as given above and  $R_{12}$  is hydrogen or trimethylsilyl group).
  - [14] A Sym-halo-triindole derivative represented by the following general formula (13)

[formula 32]

$$X \longrightarrow X$$

$$X \longrightarrow X$$

$$R_{10} \longrightarrow X$$

$$R_{10} \longrightarrow X$$

$$X \longrightarrow X$$

$$X$$

10 (wherein  $R_{10}$  is C2-C12 alkyl group, substituted C2-C12 alkyl group, C2-C12 haloalkyl group or aryl C1-C6 alkyl group; and X is halogen).